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Adapting current model with field data of related performance reference compounds in passive samplers to accurately monitor hydrophobic organic compounds in aqueous media

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Abstract Performance reference compounds (PRCs) are neutral organic compounds, introduced in a passive sampler prior deployment for the assessment of in situ sampling rate. In this study, evaluation of in situ sampling rates of 16 ^{13}C-PAH-PRCs with moderate and high hydrophobicity was established to provide an overall correction factor for variations in virtual organism (VO) uptake rates of the analytes of interest. In situ sampling rate was compared to an empirical model during sampling campaign in 2011 with VO in 12 different sites along the Three Gorges Reservoir (TGR) in China. A discrepancy was observed for high hydrophobic compounds with log K_{ow} ranging from 5.18 to 6.63 where ΣPAH concentration in TGR from Huckins model (305,624 pg/L) was resulted to be roughly 2-fold higher than the alternative procedure (182,292 pg/L). A relationship between in situ sampling rates of the 16 ^{13}C-PAH-

PRCs (Rs,$_{PRC}$) and log K_{ow} was set up to allow then calculation of analyte sampling rate Rs$_{analyte}$(N) of various organic pollutants with log $K_{ow} \leq 6.63$.

Introduction

A virtual organism (VO) is defined as artificial property-tool, reflecting exposomic processes in compartments (fat, protein, membranes, etc.) of real organisms (Schramm et al. 2013). In this study, the VO is the semipermeable membrane device (SPMD). The basic theory of this passive sampler in water developed by Huckins et al. (1993) is used to determine the amount of freely dissolved nonpolar organic chemicals for in situ monitoring trace levels. The target compounds are accumulated in VO from their freely dissolved form in water. Hence, the transient cross-section of the polymeric membrane, which maximal diameter is about 10 Å, does not restrict the passage of these respective compounds. The transport mechanism from the water phase to the VO is limited either by diffusion under water boundary layer (WBL) control or by the resistance in the membrane of VO. The WBL is a thin hydrodynamically complex region area between the VO membrane and the water body from the bulk water, created by molecules which cannot pass through the membrane.

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Under membrane control, VO acts as permeate sampler and analyte sampling rates increase with octanol-water partition coefficient K_{ow}, while under WBL, VO acts as diffusion sampler and the sampling rates remain constant or slightly increase with K_{ow} (Huckins et al. 2006a; Lohmann et al. 2012). The turning point between membrane and boundary layer rate control depends on flow and turbulence conditions at the external surface of the membrane. Booij et al. (1998) included performance reference compounds (PRCs) to compensate for environmental factors that can affect uptake kinetics of SPMD. Thus, a high turbulence leads to more release of PRC and therefore to a higher sampling rate. PRCs are analytically non-interfering compounds. They are not present in the environment and are spiked into passive samplers during their production (Huckins et al. 2002a, 2002b; Booij et al. 2007b). The PRC method relies on isotropic exchange so that the uptake of the target analyte into the sorbent phase is presumably synchronized with the dissipation of preloaded PRCs out of the sorbent phase. Thus, PRC loss rate data can be used to adjust VO-derived estimates of ambient concentrations to reflect site-specific environmental conditions of an exposure. Huckins et al. (2002a) have established a model to estimate analyte sampling rate $Rs_{analyte}(H)$ by using PRCs. This model is based on the fact that hydrophobic compounds in VO with different log K_{ow} values can adjust for each other as long as the uptake mechanism is the same. Huckins demonstrated that VO kinetic exchange of hydrophobic compounds with high log $K_{ow} \geq 4.4$ are generally under water boundary control (Huckins et al. 1999) and the effects of environmental variables on the pollutant exchange rates with a wide range of K_{ow} 's is concluded as constant (Booij et al. 1998; Huckins et al. 2002a). However, the model of Huckins may be inappropriate if the uptake mechanism of the target compound is under membrane control while the chosen PRC release is under WBL control. Furthermore, the change of exposure scenarios is not only limited to environmental variables but also to chemical properties of organic pollutants. Studies found size-disparity effect in the polymer triolein on organic compounds (Chiou 1985) which may affect the mass transfer lipid-membrane during molecular exchange and allow then membrane control of high molecular weight rather than WBL control as expected. The model of Huckins consisted of extrapolation of analyte sampling rate with values derived from laboratory calibration studies and a chosen PRC limited to a criterion of

arbitrary values from 20 to 80% losses to minimize propagation of errors from subtracting two large numbers. Tomaszewski and Luthy (2008) referred to Huckins method, used a single PRC to investigate a suite of PCBs with PE sampler in pore water, and came to the conclusion that, after 28 days of deployment, this approach matched field-measured uptake rates for most congeners but tended to underestimate uptake rates for higher molecular weight compounds. Liu et al. (2013) suggested that the use of individual PRC to estimate a group of analyte may affect the quantitation because of their slight differences in physicochemical properties or in retention mechanisms, especially for high hydrophobic compounds. Hence, there is a gap in the Huckins method between theory and experimental sampling rates. Their limit can be observed on high hydrophobic compounds since these compounds are most often adsorbed to dissolved organic carbon (DOC) (Lundqvist 2011). Augulyte and Bergqvist (2007) have investigated on the monitoring of high hydrophobic compounds with VO and came to the conclusion that fouling such as sludge particles, fat, and salt particles can influence the thickness of the water boundary layer (WBL) on the surface of the membranes VO, thus can affect uptake rate of high molecular weight compounds with high log K_{ow}.

The purpose of this study is to use a group of labeled PAH-PRCs with log K_{ow} range from 3.38 to 6.63 to estimate in situ the target analyte sampling rate $Rs_{analyte}(N)$ and to establish a relationship between log K_{ow} and $Rs_{,PRC}(N)$ to allow the determination of accurate values of water concentration of compounds with high hydrophobicity. Aforetime, we aimed to evaluate 16 ^{13}C PAH-PRC behavior using information from previous sampling campaigns (Wang et al. 2009; Karacık et al. 2013; Wang et al. 2013).

Materials and methods

The term SPMD was replaced in this study with virtual organism (VO) due to other dimensions of the samplers. In comparison with the mass fraction of 20% triolein of a standard SPMD, the mass fraction of VO is 44% to gain more power for the accumulation and thus determination of lipophilic compounds per sampler. This is meant to improve the sensitivity for the chemicals under investigation and achieve better results. The description of VO preparation, information

on the different sample sites and details regarding extraction, clean-up, and analysis of samples were presented in previous publications (Wang et al. 2009; Karacık et al. 2013; Wang et al. 2013) and are briefly described in supporting information.

Huckins model

The concentration of freely dissolved nonpolar organic compounds is difficult to evaluate directly in a water sample as most of these hydrophobic substances will be associated to DOC. This concentration in VO (C_{VO}) was quantified after laboratory extraction by Huckins et al. (2006b) and described as:

$$C_{VO} = K_{VO\_W} C_W [1 - \exp(ke_{,PRC} t)] \quad (1)$$

where K_{VO_W} is the VO-water partition coefficient (L.L^{-1}), C_W is the analyte concentration in water, and $ke_{,PRC}$ is the elimination rate constant of corresponding PRC per day (d^{-1}). To mitigate susceptible environmental factors, the PRCs are used to determine the elimination rate $ke_{,PRC}$ of the native compound of interest. Under conditions of isotropic exchange, $ke_{,PRC}$ can be described at each sampling site by the following relationship:

$$ke_{,PRC} = -\frac{\ln\left(N_{t,PRC}/N_{0,PRC}\right)}{t} \quad (2)$$

where $N_{0,PRC}$ is the retained PRC fraction at the beginning of the exposure period and $N_{t,PRC}$ is the retained PRC fraction after the exposure period t. From the equation (1), it was assumed that equilibrium in VO was reached when $ke_{,PRC} \, t \geq 1$ and C_{VO} increased linearly with time when $ke_{,PRC} \, t < 1$. Using PRC data after deployment time, Huckins et al. (2006b) defined the PRC-based sampling rate $Rs_{,PRC}$ (L.d^{-1}) as:

$$Rs_{,PRC} = Vs \cdot K_{VO\_W} \cdot ke_{,PRC} \quad (3)$$

Vs is the VO volume (L).

The equation of analyte sampling rate proposed by Huckins $Rs_{analyte}$ (H) is applied when exchange kinetic is under WBL control and is determined using experimentally values as following:

$$Rs_{analyte}(H) = Rs_{,PRC} \cdot \left(\frac{Vm_{PRC}}{Vm}\right)^{0.39} \quad (4)$$

Vm_{PRC} is the LeBas molar volume of the selected PRC and Vm is the molar volume of the target analyte.

Analytes sequestered by the VO may be in the linear uptake (integrative) sampling, curvilinear, or equilibrium partitioning sampling phases. A model to calculate water concentration was introduced by Huckins et al. (2006b) and can be used regardless of whether the analyte's uptake is in a linear, curvilinear, or equilibrium phase together in combination with $Rs_{analyte}$, K_{VO_W}, and N_{VO}, the absorbed amount of organic compound after exposure time t.

$$C_w = \frac{N_{VO}}{V_s \cdot K_{VO\_W} \left(1 - \exp\left(-\frac{R_{Sanalyte} \cdot t}{Vs \cdot K_{VO\_W}}\right)\right)} \quad (5)$$

To evaluate K_{VO_W} with 44% triolein, the theory of Mackay and Paterson (1982) has been used: the low-density polyethylene (LPDE) and triolein are considering two compartments, in which the solute has different concentration and fugacity. The resistance is controlled by the boundary layer and equilibrium exists between the membrane (LPDE) and lipid (triolein) phases (Gale 1998). K_{VO_W} (VO with triolein mass 44% of total mass, resp. volume due to nearly identical densities) is represented as:

$$K_{V0-W} = \frac{K_{T.W} \cdot V_T + K_{LPDE.W} \cdot V_{LPDE}}{V_T + V_{LPDE}} \quad (6)$$

V_T is the volume of the triolein (L), V_{LPDE} the volume of LPDE (L), $K_{T.W}$ is the triolein-water partitioning coefficient (L.L^{-1}), and $K_{LPDE.W}$ is the LPDE-water partitioning coefficient (L.L^{-1}). Chiou (1985); Booij and Smedes (2010) established a close correlation between, respectively, $K_{T.W}$, $K_{LPDE.W}$, and K_{ow} with $3 < \log K_{ow} < 7$:

$$\log K_{T.W} = 1.00 \log K_{ow} + 0.105 \quad (7)$$

(Chiou 1985)
and

$$\log K_{LPDEW} = 1.05 \log K_{ow} - 0.59 \quad (8)$$

(Booij and Smedes 2010).

Kow is the octanol-water partitioning coefficient (L.L^{-1}).

New calculation model for the estimation of sampling rate $Rs_{analyte}(N)$

The alternative calculation model is based on the use of all in situ PRC data, including those whose PRC

concentration remaining are close to the limit of detection LOD and those whose PRCs are non-depleted.

Some high hydrophobic compounds presented values of $Rs_{,PRC}$ (see Eq. 3) around zero because of their low retention in VO. In this case, uncertainty values were used to estimate the minimal sample rate R_{min}.

To obtain the maximal PRC retained in VO analytical uncertainty and thus the maximal possible loss of PRC due to analytical performance, the measure of 12 replicated VO, placed in a glass vial, hermetically closed with the cap and exposed in the field atmosphere, was achieved (Fig. 1).The Student t distribution was used to obtain confidence limits for measurement uncertainty (See supplementary information for more details). The uncertainty (y) of the VO-field blanks was given as:

$$y = CV - t_{\alpha,v}S_{CV} \qquad (9)$$

where $t_{\alpha,v}$ is the critical value of Student's t for the chosen α level and for $\nu = n-1$ degrees of freedom and S_{CV} is the standard error of the coefficient of variation CV.

The uncertainty value was used to obtain the maximal retained PRC concentration in percentage after exposure time:

$$u_{\max} = 100 - y \qquad (10)$$

u_{max} was used to determinate the maximum elimination rate ke_{max}

$$ke_{\max} = -\frac{\ln\left(u_{\max}/u_0\right)}{t} \qquad (11)$$

u_0 is the retained PRC concentration in percentage at time 0.

The minimal expected sampling rate (Rs_{min}) was thereby deduced.

$$R_{S\min} = VsK_{VO\_W}ke_{\max} \qquad (12)$$

R_{Smin} was applied as the new values of PRC sampling rate $Rs_{,PRC}(N)$ if a direct measurement was not obtainable.

A relation between $Rs_{,PRC}(N)$ of the 16 ^{13}C PRC-PAH and log K_{ow} was applied to allow the estimation of the sampling rate of other groups of organic pollutants $Rs_{analyte}(N)$ such as OCPs and PCBs, independently whether the kinetic exchange was under membrane control or under WBL control. This relation was presented as an exponential function form with a correlation coefficient $R^2 > 0.75$. The sampling rates among studies appeared to be shifted by relatively constant factors a and b. A fitted model relation in this field condition is giving as:

$$Rs_{analyte}(N) = ae^{b\log K_{ow}} \qquad (13)$$

where a and b are constants for a given exposure, but may vary among exposures according to differences in hydrodynamical conditions and sampler geometry.

Results and discussion

Evaluation of PRC-PAH releases

Field data from previous sampling campaign (Wang et al. 2009; Karacık et al. 2013; Wang et al. 2013) reveal that the release of the 16 PRC-PAHs into VO in the water media was observed, independently of environmental conditions. Relation between the concentration

Fig. 1 Schema representing uncertainty field y of dissipated PAH-PRC values (u) during exposure times. $u_{\max}$ is the largest possible deviation from the average dissipation of a PRC which does not exhibit significant dissipation after a certain sampling period. $u_{\max}$ can be used to estimate the minimal possible sampling rate for such compounds
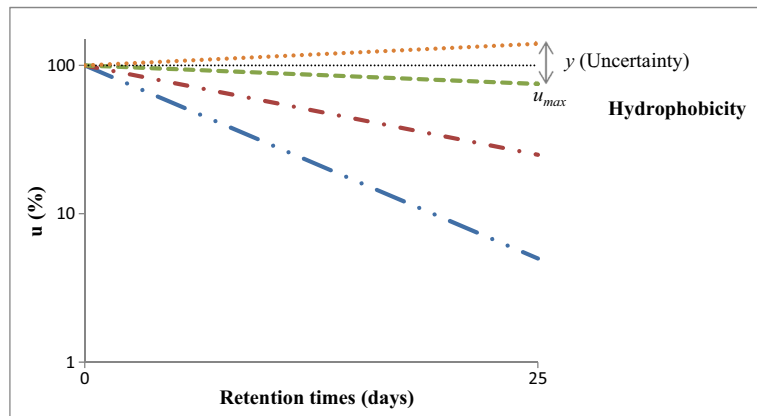
and time was described by a log-linear empirical function (Fig. 2) where the slope is referred to as the PRC elimination rate constant ($ke,_{PRC}$) in Eq. (2). Naphthalene-$^{13}C_6$ with log K_{ow} = 3.38 presented the highest $ke,_{PRC}$ value with 0.24 d^{-1}, while Indeno(1,2,3-c,d)pyrene-$^{13}C_6$ with log K_{ow} = 6.42 presented the lowest $ke,_{PRC}$ value with 0.01 d^{-1}. Thus, the elimination rate ($ke,_{PRC}$) increased with the decreased log K_{ow}.

Using Eq. (1), naphthalene-$^{13}C_6$ and acenaphtylene-$^{13}C_6$ attained equilibrium with $ke,_{PRC}\ t > 1$ for an exposure time of 30 days while the others compounds were still in the linear stage with $ke,_{PRC}\ t < 1$ (Huckins et al. 2006b). Compounds with lower molecular weight than fluoranthene-$^{13}C_6$ presented relevant values of $ke,_{PRC}$, whereas higher molecular weight with log K_{ow} range 5.18 to 6.63 did not perform well for this short period of deployments as they presented a very low $ke,_{PRC}$, ranging from 0.02 to 0.01 d^{-1}. These results were in accordance with the U.S. Environmental Protection Agency (EPA 2009) suggesting that log K_{ow} values are generally inversely related to aqueous solubility and directly proportional to molecular weight. Huckins et al. 2002a

advised to exclude the high molecular weight compounds with log $K_{ow} > 5.5$ for obtaining measurable losses of PRCs. He referred therefore in its model one PRC with low to moderate molecular weight to estimate sampling rate of high molecular weight compounds. However, the 16 PRCs with low to high molecular weight were presented in different kinetic stage after exposure; the choice of one PRC to reflect the loss rate of a wide range of target chemical may be inappropriate as there was a high risk that the analyte did not have a diffusion and sorption matching PRC. Besides, the obtaining of low PRC elimination rate $ke,_{PRC}$ for compounds with log $K_{ow} > 5.18$ did not mean that there was no isotropic exchange between high hydrophobic PRC compounds and their native analogues.

$Rs_{PAH}(N)$ estimation procedure with sixteen PAH-PRCs during sampling campaign in Three Gorges Reservoir in 2011

During sampling campaign in 2011 (Wang et al. 2013), VO was deployed in 12 sampling sites along the Three
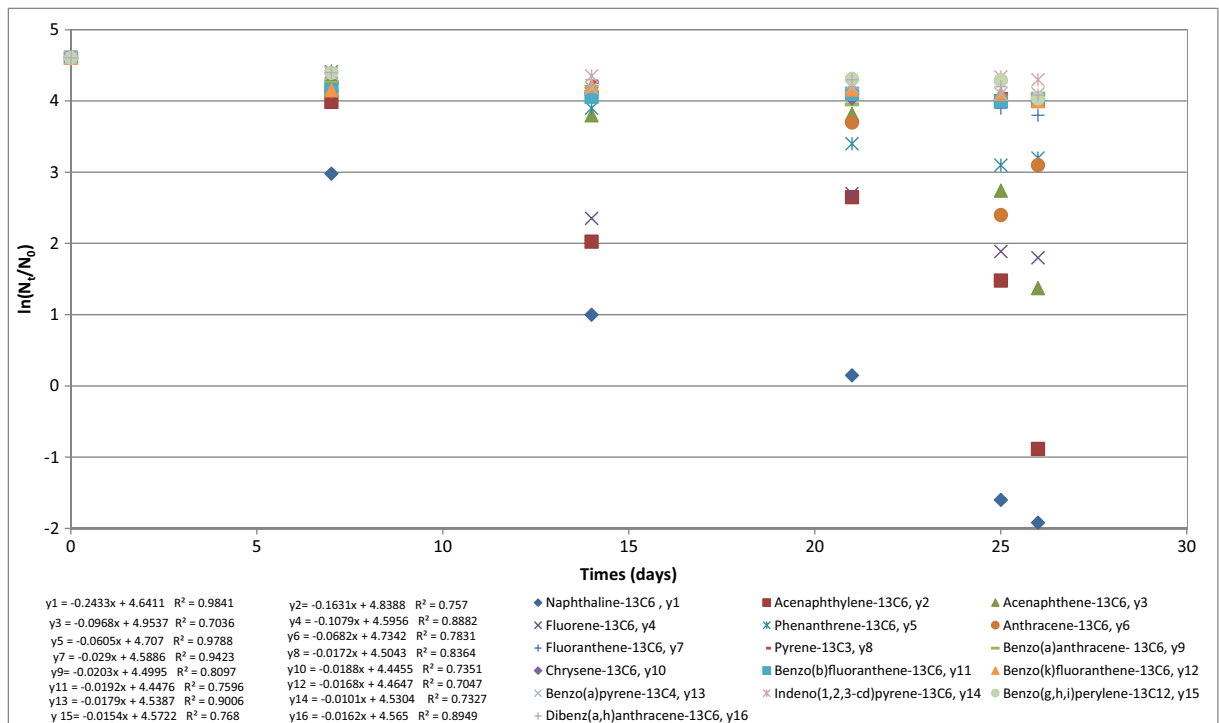

y1 = -0.2433x + 4.6411   R² = 0.9841
y3 = -0.0968x + 4.9537   R² = 0.7036
y5 = -0.0605x + 4.707   R² = 0.9788
y7 = -0.029x + 4.5886   R² = 0.9423
y9= -0.0203x + 4.4995   R² = 0.8097
y11 = -0.0192x + 4.4476   R² = 0.7596
y13 = -0.0179x + 4.5387   R² = 0.9006
y 15= -0.0154x + 4.5722   R² = 0.768

y2 = -0.1631x + 4.8388   R² = 0.757
y4 = -0.1079x + 4.5956   R² = 0.8882
y6 = -0.0682x + 4.7342   R² = 0.7831
y8 = -0.0172x + 4.5043   R² = 0.8364
y10 = -0.0188x + 4.4455   R² = 0.7351
y12 = -0.0168x + 4.4647   R² = 0.7047
y14 = -0.0101x + 4.5304   R² = 0.7327
y16 = -0.0162x + 4.565   R² = 0.8949

◆ Naphthaline-13C6 , y1   ■ Acenaphthylene-13C6, y2   ▲ Acenaphthene-13C6, y3
✕ Fluorene-13C6, y4   ✕ Phenanthrene-13C6, y5   ● Anthracene-13C6, y6
+ Fluoranthene-13C6, y7   - Pyrene-13C3, y8   — Benzo(a)anthracene- 13C6, y9
◆ Chrysene-13C6, y10   ■ Benzo(b)fluoranthene-13C6, y11   ▲ Benzo(k)fluoranthene-13C6, y12
✕ Benzo(a)pyrene-13C4, y13   ✕ Indeno(1,2,3-cd)pyrene-13C6, y14   ● Benzo(g,h,i)perylene-13C12, y15
+ Dibenz(a,h)anthracene-13C6, y16

Fig. 2 Exposure time as a function of retained PRC at time t N of 16 PAH-PRCs with log K_{ow} range 3 to 6.63: Naph-$^{13}C_6$, Acy-$^{13}C_6$, Ace-$^{13}C_6$, Fle-$^{13}C_6$, Fen-$^{13}C_6$, Ant-$^{13}C_6$, Flo-$^{13}C_6$, Pyr-$^{13}C_3$, BaA-$^{13}C_6$, Chr-$^{13}C_6$, BbF-$^{13}C_6$, BkF-$^{13}C_6$, BaP-$^{13}C_4$, IND-$^{13}C_6$, BghiP-$^{13}C_{12}$, and DahA-$^{13}C_6$. Collected data points represent measurements within three different studies with an exposure times from 7 to 30 days (Wang et al. 2009, 2013 and Karacık et al. 2013)

Gorges Reservoir (TGR) for 26 days (Fig. S1). Twelve VO-field blanks were used for the estimation of uncertainty y, using Eq.S5. Uncertainty values of each individual PAH-PRC were given at 95% level of confidence interval. These values provide the maximum retained PAH-PRCs u_{max} (Eq. 10) in blank VO sample that lead to a minimum sampling rate Rs_{min} (Eq.12). Rs_{min} was estimated for each sampling sites, depending on K_{VO_W} and Vs of VO. Table 1 presented the estimation of Rs_{min} of the 16 ^{13}C-PRC-PAH in Maoping near Three Gorges Dam (TGD) and the values ranged from 0.004 L.d^{-1} for Nap-^{13}C$_{12}$ to 14.310 L.d-1 for BghiP-^{13}C$_{12}$. Rs_{min} was used to obtain determinable value of $Rs,_{PRC}(N)$ (Table S1).

$Rs,_{PRC}(N)$ of the 16 ^{13}C PAH-PRCs were directly used as the native PAHs sampling rates $Rs,_{PAH}(N)$ with similar physicochemical properties. The result was summarized in Table 2 and shows increasing values of $Rs,_{PAH}(N)$ from 0.67 L.d^{-1} for Nap in Maoping to 151.52 L.d^{-1} for DahA in Chongqing. This significant variation was clearly due to the difference of exposure conditions at the various sampling sites. $Rs,_{PAH}(N)$ increment for high hydrophobic compounds were observed at each sampling site regardless of physical conditions. The contrast of the exchange kinetic between

moderate and high hydrophobic PRCs into VO may be due to a potential perturbation during molecule transport or to dissimilarity affinities to LPDE membrane between PRC and target analyte, so that the resistance was controlled by the membrane instead of WBL according to Huckins theory. This suggestion is consistent with a previous study (Luellen and Shea 2002) that found that the assumption that the WBL is controlling during transport may not be true for high hydrophobic PAHs. Furthermore, previous studies suggested that membrane permeability limitation should be a factor for high hydrophobic PAHs with dimension $\geq$ 10 Å, which is more than the maximal pore diameter of the LPDE (Meadows et al. 1998; Rusina et al. 2010). Thus, some of the high lipophilic compounds can only pass the pore diameter of LPDE in one of its dimensions. This theory is somehow compatible with the results observed in VO from our new method of calculation and it is one of the explanation why using a single PRC to estimate concentration of a group of compounds as Huckins method can be unfounded.

Some chemical factors have a significant influence on uptake kinetics of high log K_{ow} into VO. Lipophilic compounds are preferentially sorbed to DOC in water column and the main chemical characteristic of these

Table 1 Rs_{min} of ^{13}C-PRC-PAH are estimated after a deployment time of 26 days in Maoping. The uncertainty y (%) is used to obtain the maximal dissipation rate capacity ke_{max}. Log K_{ow} values of unlabeled PAHs from Huckins et al. (2004)

PRC-PAHs	Log K_{ow}	Vm cm^3/mol	Sn –	$\bar{u}$ %	CV %	S_{CV} %	$t\alpha,\nu\ S_{CV}$ %	$CV- t\alpha\nu S_{CV}$ %	u_{max} %	ke_{min} d^{-1}	Rs_{min} L.d^{-1}
Nap-^{13}C$_6$	3.38	147.6	6	97	6	1.26	2.78	3.41	97	0.001	0.004
Acy-^{13}C$_6$	4.07	165.7	8	96	8	1.70	3.74	4.58	95	0.002	0.026
Ace-^{13}C$_6$	3.92	173.1	10	100	10	2.04	4.49	5.51	94	0.002	0.022
Fle-^{13}C$_6$	4.1	187.9	10	104	9	1.87	4.11	5.04	95	0.002	0.030
Phe-^{13}C$_6$	4.46	199.2	8	92	9	1.75	3.84	4.71	95	0.002	0.066
An-^{13}C$_6$	4.54	196.7	14	110	13	2.56	5.63	6.91	93	0.003	0.117
Flu-^{13}C$_6$	4.84	217.3	4	93	4	0.78	1.71	2.09	98	0.001	0.070
Pyr-^{13}C$_3$	5.18	213.8	5	96	5	0.97	2.14	2.62	97	0.001	0.194
BaA-^{13}C$_6$	5.6	248.3	8	99	8	1.69	3.72	4.56	95	0.002	0.911
Chr-^{13}C$_6$	5.84	250.8	8	101	8	1.54	3.39	4.16	96	0.002	1.451
BbF-^{13}C$_6$	6.44	268.9	8	98	8	1.60	3.52	4.31	96	0.002	6.129
BkF-^{13}C$_6$	6.44	268.9	8	98	8	1.61	3.55	4.35	96	0.002	6.189
BaP-^{13}C$_4$	6.42	262.9	8	98	9	1.74	3.83	4.70	95	0.002	6.385
InD-^{13}C$_6$	6.42	283.5	7	92	8	1.64	3.62	4.43	96	0.002	6.015
BghiP-^{13}C$_{12}$	6.63	277.5	4	35	12	2.37	5.21	6.39	94	0.003	14.310
DahA-^{13}C$_6$	6.5	299.9	9	94	9	1.90	4.18	5.13	95	0.002	8.418

Table 2 The 16 native PAH sampling rate $Rs_{PAH}(N)$ values (L.d^{-1}) of compounds with log K_{ow} ranging from 3.38 to 6.63 at 12 different sites across the Three Gorge Reservoir using in situ sampling rate of their analogue PRCs. Estimated values of $Rs_{PAH}(N)$ for some compounds fail because their PRCs, presented a total dissipation in VO during the 26 days of deployment

PRC-PAHs	Maoping	Guojiaba	Xiangxi I	Xiangxi II	Daning I	Daning II	Fendji	Xiaojiang I	Xiaojiang II	Wanzhou	Changshou	Chongqing
Nap	0.67		0.73	0.73								0.73
Acy	1.71	3.04	2.45	2.74			3.04	3.07	2.96	2.03	1.65	3.11
Ace	0.74	1.54	1.17	1.15		1.43				0.98	1.08	1.31
Fle	1.09	2.03	2.10	2.58	2.57	2.96	2.37	2.41	2.37	1.52	1.99	3.03
Phe	1.46	2.15	2.42	2.87	3.08	3.05	2.89	2.93	2.94	1.83	2.24	6.20
An	1.58	2.31	2.51	2.97	3.27	3.18	3.19	3.22	3.25	2.03	2.41	7.91
Flu	1.12	2.04	1.40	1.59	1.71	1.36	1.63	1.47	1.46	1.66	1.09	6.63
Pyr	1.76	2.45	4.14	2.74	2.76	3.54	2.93	2.92	2.76	2.43	2.20	2.23
BaA	4.57	3.02	3.25	2.75	3.25	5.92	4.06	4.91	4.92	4.95	4.95	11.30
Chr	8.85	8.01	7.07	4.82	9.59	10.46	8.47	8.84	8.47	8.51	8.51	38.58
BbF	33.75	12.24	27.00	16.54	6.17	16.17	16.21	16.13	16.19	6.36	7.84	109.62
BkF	32.12	19.41	22.29	17.75	6.23	16.23	19.49	16.19	16.25	6.42	10.07	41.97
BaP	30.89	33.97	25.26	8.23	9.43	18.21	17.08	16.38	12.66	6.62	100.44	74.64
InD	21.25	17.91	6.15	6.12	6.06	6.06	6.09	6.01	6.08	6.24	22.68	18.65
BghiP	57.91	127.07	69.53	53.73	10.83	43.24	28.77	14.31	14.46	14.84	63.28	116.98
DahA	29.83	11.57	22.26	14.77	8.48	9.45	8.53	8.42	8.51	8.73	28.53	151.52

compounds that contributes to the association with DOC is their hydrophobicity. However, VO only accumulates the freely existing compounds in aqueous systems and not the fraction of DOC-bound compound (Rusina et al. 2009). In the field, DOC can associate with the membrane and can cause alternation of the elimination or uptake rate constant of high hydrophobic contaminant (Ke et al. 2007). This observation further indicates that the application of one PRC as reported by Huckins et al. (1993) to calibrate a suite of analytes may lead to an underestimation of uptake rate of high K_{ow} compounds. Therefore, it is important for field studies to use a representative variety of PRCs similarly to the targeted chemicals.

The salinity can also affect the uptake of high hydrophobic compounds and can cause a bias of the result if only one PRC compounds is used. Brown and Weiss (1978) demonstrated that water-quality variables, such as salinity, can affect the dissolved concentrations of hydrophobic compounds in environmental waters and studies have shown that the salinity in some places of the water resources areas in TGR, during periods in dry season, could exceed the standard (0.25‰) with a salinity value greater than 0.48‰ (Baodong et al. 1999; HSU et al. 1999; An et al. 2009).

A relationship between $Rs_{PRC}(N)$ and log K_{ow} was established (Table 3 and Fig. S3). This equation is defined to extrapolate a large number of PRCs with moderate to high log K_{ow} to insure an accurate value of the

water concentration of analyte with high hydrophobicity such as OCPs and PCBs (Temoka et al. 2016).

Comparison between $Rs_{PAH}(N)$ and $Rs_{PAH}(H)$

The in situ PAH-PRC sampling rate $Rs_{PAH}(N)$ from Table 2 was used in comparison with the experimental PAH sampling rate $Rs_{PAH}(H)$ from the WBL controlled uptake method of Huckins (Eq. 4). PRC-Flu-$^{13}C_6$, with a loss between 20 to 80%, was selected according to the criteria reported by Huckins et al. (2002a). The result yields to a slight decrease of $Rs_{PAH}(H)$ at different log K_{ow} values ranged from 3.38 to 6.63 (Fig. 3 and Fig. S4). The diffusion was suggested to be under WBL control, so the VO acted as a diffuse sampler. In opposite, $Rs_{PRC}(N)$ of compounds with 3.38 > log K_{ow} < 5.18 presented values that were generally similar to those obtained using the empirical model from Huckins, whereas a significant deviation for compounds with 5.18 > log K_{ow} < 6.63 was observed. On the one hand, membrane diffusion could be an explanation of this observation. Under chemical conditions, as demonstrated above, rate control may have switched from WBL to membrane for highly hydrophobic compounds. The VO acts, in this case, as a permeate sampler. On the other hand, the significant deviation is in agreement with the theories of Vrana and Schüürmann (2002), Luellen and Shea (2002) and Booij et al. (2007a) suggesting that under water boundary layer control in SPMD, the sampling rates of compounds increase with increasing log K_{ow} and a maximum value in sampling rate is reached for compounds with log K_{ow} value at around six. The

Table 3 Equation of extrapolation of $Rs_{PRC}(N)$ and log K_{ow} (x) to estimate $Rs_{analyte}(N)$ of various organic pollutants such as PCBs and OCPs

| Sampling sites	$Rs_{analyte}(N)$	
Maoping	$y = 0.0033e^{1.3863x}$	$R^2 = 0.916$
Guojiaba	$y = 0.017e^{1.0929x}$	$R^2 = 0.7454$
Badong I	$y = 0.017e^{1.087x}$	$R^2 = 0.8253$
Badong II	$y = 0.0422e^{0.8835x}$	$R^2 = 0.7595$
Daning I	$y = 0.215e^{0.5509x}$	$R^2 = 0.7012$
Daning II	$y = 0.0453e^{0.8927x}$	$R^2 = 0.7591$
Fendji	$y = 0.0713e^{0.8024x}$	$R^2 = 0.7393$
Xiaojiang I	$y = 0.1037e^{0.7247x}$	$R^2 = 0.7498$
Xiaojiang II	$y = 0.1063e^{0.7156x}$	$R^2 = 0.7588$
Wanzhou	$y = 0.0676e^{0.7403x}$	$R^2 = 0.8792$
Changshou	$y = 0.0074e^{1.2374x}$	$R^2 = 0.7636$
Chongqing	$y = 0.0074e^{1.4007x}$	$R^2 = 0.8513$
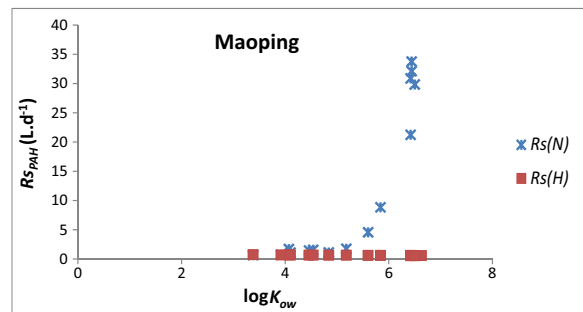
Fig. 3 Comparison between $Rs_{PAH}(N)$ and $Rs_{PAH}(H)$ (L.d^{-1}) as a function of log K_{ow} from ranging from 3.38 to 6.5 of 16 ^{13}C PRC-PAHs. The sampling site was in Maoping (near the dam) at 17.3 ± 4 °C after 26 days of deployment. $Rs_{PAH}(H)$ remains constant for compounds with log K_{ow} values range from 3.38 to 6.63 while $Rs_{PAH}(N)$ increases significantly for compounds with log K_{ow} values range from 5.18 to 6

fact that there was no maximum observed for $Rs_{PRC}(N)$ were likely due to the mass fraction of triolein (44%) in this passive sampler VO, higher than the standard mass fraction of Huckins (20%) in SPMD. The high volume of triolein in VO had affected the sampling rate in such a way that its maximum was postponed to compounds with log $K_{ow} > 6$. In accordance with the result on the PRC evaluation (III.1), Acy is expected to be in equilibrium stage after 26 days of exposure. In this case, Huckins et al. (2006b) demonstrate that the concentration in the water phase can be calculated with the partition coefficient K_{VO_W} (L.L^{-1}), the amount of analyte accumulated after a given exposure time N (mass) and the volume of the receiving phase V_S (L) giving as:

$$Cw_{eq} = \frac{N}{Vs\, K_{VO\_W}} \tag{14}$$

or with $Rs_{analyte}(N)$(L.d^{-1}), giving as:

$$Cw_{Rs} = \frac{N}{Rs_{analyte}(N)\, t} \tag{15}$$

To check $Rs_{PRC}(N)$ values, both calculations are made. Cw_{Rs} of Acy are expected to be equal to Cw_{eq} after 26 days in accordance with the conclusion taken above.

Results show similar values for Cw_{eq} and Cw_{Rs} (Table 4). In some cases, the remained PRC was not determinable because Acy-PRC was completely released making it impossible to calculate Cw_{Rs}.

$Rs_{PAH}(N)$ and $Rs_{PAH}(H)$ were used to estimate water concentration of high hydrophobic PAH compounds with log $K_{ow} \geq 5.18$ such as Pyr, BaA and Chr, BbF, BkF, BaP, DahA, BghiP, and inD. The result of PAHs, grouped by a ring number in compounds, presented a large discrepancy (Fig. 4). Hence, the concentration of the ΣPAH in the TGR ranged from 248 pg/L for six-ring compounds to 182,292 pg/L for four-ring compounds with the alternative model, whereas using Huckins model ΣPAH was considerably higher, ranging from 5323 pg/L for six-ring compounds to 305,624 pg/L for four-ring compounds. Both models presented a high percentage of four-ring PAHs freely dissolved in water. The difference between $Rs_{PAH}(N)$ and $Rs_{PAH}(H)$ was obvious for higher molecular weight compounds. In Huckins estimation, the six- and five-ring PAH portions were, respectively, 2 and 12%, versus 0.1 and 1% by using directly the measured in situ sampling rate. VO samples were compared to

Table 4 Comparison of water concentration (pg/L) of acenaphtylene from K_{VO_W} (Cw_{eq}) and from sampling rate Rs (Cw_{Rs})

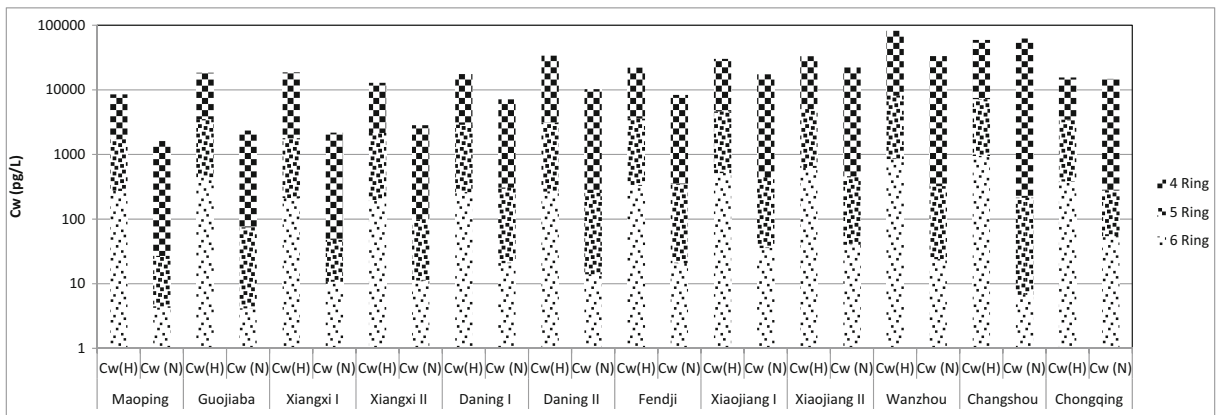|	Maoping	Guojiaba	Xiangxi I	Xiangxi II	Daning I	Daning II	Fendji	Xiaojiang I	Xiaojiang II	Wanzhou	Changshou	Chongqing
$Cw_{(eq)}$	39.11	139.67	38.24	67.70	77.44	42.65	94.57	48.91	52.90	37.65	37.65	1251.36
$Cw_{(Rs)}$	40.89	142.44	38.73	68.20	–	–	94.97	49.09	53.15	39.88	39.84	1256.53

Fig. 4 Comparison of water concentrations in pg/L, using Huckins method ($Cw(H)$) and the new procedure ($Cw(N)$), of four.-, five-, and six-ring PAHs with log K_{ow} range from 5.18 to 6.63 during 26 days of deployment (17.3–23.9 °C) at 12 different sampling sites along the Three Gorges Reservoir

XAD cartridges for active sampling at the same period near TGD in Maoping. The concentration data evaluated by this type of sampling self-packed XAD cartridge have been already published to a large extent (Deyerling et al. 2014). Since only the freely dissolved form of a chemical is available to partition into VO membrane, an estimation of total PAH concentration in crude water was established considering also suspended particles S_{SP} and DOC (Table S2). The equations were already described in previous study (Temoka et al. 2016). The mean value of daily discharge of DOC (1.6 mg C/L) in Yichang, determined by Müller et al. (2008), was used for the calculation. For the simplification of the estimation of different masses constitutions, all densities δ were considered 1 kg/L. The result of total PAH concentration found in the filter cartridge was 12.38 ng L^{-1} (Table 5) which was slightly lower than the concentration from new method VOs(N) with 21.48 ng/L and 3-fold lower than the concentration from Huckins method VOs(H) 44.89 ng/L. Although the sampling cartridge was generated within about 2 h on two consecutive days, the large sampling volume of about 400 L helped to compensate this disadvantage and to generate representative average samples. Similarities in the concentration were observed between VOs(N) and XAD cartridge of 5-ring PAHs with a mean value of 2.12 and 2.82 ng/L, respectively, and of 6 ring-PAHs with mean value of 1.10 and 1.57 ng/L, respectively. VOs(H) presented around 4-3-fold higher concentration values for 5-ring PAHs (8.67 ng/L) and 6-ring PAHs (3.85 ng/L). Consequently, the cartridge measurements further support the assumption that the new VO calculation method

described in this study is more reliable than the Huckins method. Uptake rates of PAHs begin to decrease in VO when log $K_{ow} \geq 5.18$ presumably due to steric hindrance in the membrane. Thus, the assumption that log $K_{ow} \geq 4.4$ are generally under water boundary control as suggested Huckins may not be true for PAHs. This explains the discrepancy of high PAHs concentration between VOs(H) and VOs(N).

Table 5 PAHs water concentration in Maoping, determinated with new method calculation VOs(N), with Huckins method VOs(H) and from XAD cartridge (ng/L)

Analytes	VOs(H)	VOs(N)	XAD
Nap	10.27	9.07	–
Acy	0.07	0.04	0.03
Ace	0.25	0.21	0.08
Fle	1.20	0.81	0.31
Phe	7.48	2.50	1.19
An	0.72	0.31	0.28
Flu	3.24	1.56	2.30
Pyr	5.50	1.69	1.68
BaA	0.96	0.91	0.90
Chr	2.69	1.16	1.23
BbF	3.93	1.19	1.38
BkF	1.61	0.23	0.40
BaP	1.69	0.61	0.87
InD	1.91	0.72	0.66
BghiP	1.94	0.38	0.91
DahA	1.44	0.09	0.17
Σ PAHs	44.89	21.48	12.38

Conclusion

The molar volume Vm approach used by Huckins to describe the profile of $Rs_{analyte}(N)$ is not satisfying because data in field studies do not sufficiently follow the correction by molar volume. When using a single PRC to calibrate a suite of target analytes with a wide range of K_{ow} as referred to Huckins model, the retention mechanisms of all the target analytes may not necessarily be identical.

The use of the calculation procedure presented herein allows the estimation of in situ $Rs_{analyte}(N)$ of pollutants with moderate to high log K_{ow} by employing a wide range of PRCs, in order to improve the accuracy of the estimated water concentration. The model is independently to the resistance to the mass transfer across the VO membrane.

Under water boundary WBL control, $Rs_{analyte}(N)$ values were expected to gradually decline due to a small reduction in diffusion coefficient Dw (Rusina et al. 2010; Vrana et al. 2007) following the mass transfer coefficient model from Huckins et al. (2006b). Field application of VO revealed that transport of PRC compounds Naph-13C6, Acy-13C6, Ace-13C6, Fle-13C6, Fen-13C6, Ant-13C6, and Flo-13C6 with a slight variation of $Rs_{analyte}(N)$ follow the approach of Huckins. Differences for highly hydrophobic compounds (log $K_{ow} \geq 5.18$) not identical with the used PRC may be either cause by membrane permeability limitations or by deviated WBL control. Hence, low log K_{ow} PRC compounds referenced to high log K_{ow} analytes can lead to an overestimation of the analyte's water concentrations by orders of magnitude.

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